

Perspective: parameters in a self-consistent field theory of multicomponent wormlike-copolymer melts

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Abstract. We review a formalism that can be used to calculate the microphase-separated crystallographic structures of multi-component wormlike polymer melts. The approach is based on a self-consistent field theory of wormlike polymers where the persistence length of each component is an important parameter. We emphasize on an analysis of the number of independent parameters required to specify a problem in general, for a system that includes Flory-Huggins and Maier-Saupe energies. Examples of recent applications are also briefly demonstrated: AB homopolymer interface, AB diblock copolymers, and rod-coil copolymers.

Introduction

The foundation of a self-consistent field theory (SCFT), which is a convenient theoretical tool to describe the ordered structures of copolymer melts, contains three essential ingredients in theoretical polymer physics. a) The transformation from a particle-based microscopic formalism to a mean-field formalism enables focusing on the overall phase-separated structures. b) The statistical weight of a polymer configuration specifies the basic properties of a constituting polymer including degree of polymerization, block and branched architecture, and segment persistency. c) The segment-segment interactions are usually described by concepts such as the Flory-Huggins (FH) mixing free energy and the Maier-Saupe (MS) liquid-crystal free energy, semi-phenomenologically.

The use of a Gaussian statistical weight for a linear polymer is often referred to as the Edwards model [1]. It has a relatively simple mathematical structure, which can be used to describe a *flexible* polymer system within a length scale not far from a typical radius of gyration. For a spatially inhomogeneous polymer melt that displays a structural pattern where every component is described by a spatially varying volume fraction, another essential concept in polymer-melt physics is the incompressibility condition which states that the sum of all volume fraction is a spatially uniform constant [2]. The SCFT formalism built from these ideas supports the current theoretical and experimental understanding of many polymeric systems and

is well-documented in the literature. A significant number of researchers have contributed to this active area of research. Representatively, refs. [2–10] either give detailed derivation or review summary of this theoretical approach.

One of the length scales that characterize a wormlike polymer block is the persistence length λ , below which the polymer segment appears rigid. A properly built wormlike-polymer theory exhibits two asymptotic limits: at small λ it reduces to a theory describing *flexible* chains and at large λ it models a rodlike segment [11]. In recent years, a SCFT formalism, where the wormlike-chain model is used in b) instead of the Edwards model, has been used to study multiple-component polymer systems, including problems such as specific AB polymer blends and AB diblock copolymers where both AB polymers are assumed to have the same persistence length [12–16], and rod-coil diblock copolymer where the persistence lengths of one block is large and the other is small [17–22]. A typical probability distribution function of a constituent component depends on both spatial position, represented by a coordinate \mathbf{r} , and orientational direction, represented by a unit vector \mathbf{u} , of a polymer segment.

In the classical example of an AB diblock copolymer melt of flexible polymers having the same Kuhn length, the phase diagram can be drawn by using two reduced parameters: the reduced FH parameter χN and the overall volume fraction of one of the two types of monomers f [2, 9]. Needless to say, the persistencies of the polymer blocks introduce additional parameters that are required to specify a particular wormlike copolymer problem. In the current Perspective, we clarify the number of reduced,

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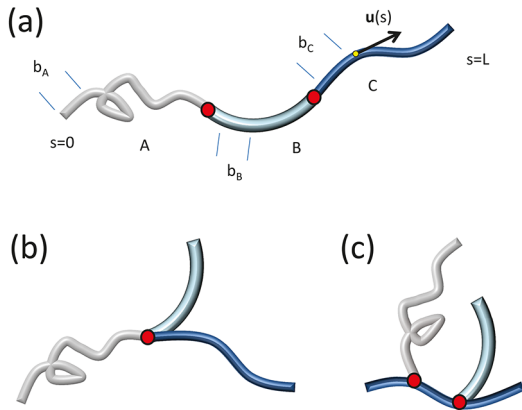


Fig. 1. Sketches for (a) linear, (b) 3-arm star, and (c) side-chain copolymer chains. Each segment is characterized by a monomeric unit of length b , which is used for volume-packing statistics, and a persistence length, which is used for conformation description.

independent parameters required to establish a phase diagram of a multi-component wormlike-polymer melt in a minimal model. In particular, we examine a polymer melt made of linearly connected blocks (an example of a tri-block polymer is shown in fig. 1(a)). Comments are made on modeling other branched structures later. An overview is given on solved and unsolved problems.

Packing of monomers

The system consists of n monodisperse linear wormlike block copolymers in volume V , where every linear chain is made of m blocks of polymers of difference species. Every polymer is modelled by a continuous space curve, where the j -th block is characterized by a bare persistence length λ_j , which specifies the orientation-orientation correlation length of a single polymer.

For the purpose of examining volume-packing of multiple polymers, we need to introduce another length scale, the segmental length b_j for the j -th block. Two such segments on different types of blocks are assumed to have the same excluded-volume effects, occupying a basic volume element ρ_0^{-1} which is block-type independent. To avoid confusion, in this Perspective we use the terminology “segment” specifically to describe such a statistical unit, not to be confused with the general meaning of “portion of a polymer”. The necessity for introduction of this length scale is evident in an extreme example of packing flexible chains (small λ) with rodlike molecules ($\lambda \gg 1$) made of monomers of similar volumes; the segmental lengths (b_j) have a similar value and the persistence lengths (λ_j) differ tremendously. Conceptually and physically these are two different length scales.

Assume that a single polymer contains a total of N_j segments of the j -th species ($j = 1, \dots, m$) and the summed total segment number $N = \sum_j N_j$. The overall volume fraction of the j -th species in the system is

$f_j = N_j/N$, where

$$\sum_{j=1}^m f_j = 1. \quad (1)$$

The total contour polymer length is then $L = \sum_j N_j b_j$. Within the summation, $N_j b_j$ is the contour length of the j -th block. A simple re-arrangement hence yields

$$\sum_{j=1}^m f_j \frac{N b_j}{L} = 1. \quad (2)$$

Note that unless b_j are all the same (when the polymers are conformationally symmetric), the volume fraction f_j is different from the length fraction $N_j b_j/L$, as different types of blocks might have different segment packing sizes. Normalization conditions (1) and (2) are independent in general.

The configuration of a typical polymer, modelled by a continuous curve, is specified by the spatial coordinate $\mathbf{R}(s)$ where s is an arcvariable that starts at one polymer end where $s = 0$ and ends at another end where $s = L$ (fig. 1(a)). Within block j , to count the number of j monomers within a polymer portion of length Δs , we use $\Delta s/b_j$, which is dimensionless. To measure the fraction of monomers within this polymer portion, using all monomers along the chain N as the base, we have $\Delta s/N b_j$, or in differential limit,

$$dt = ds/N b_j. \quad (3)$$

The ranges of variables s and t for block j are $[s_{j-1}, s_j]$ and $[t_{j-1}, t_j]$, where

$$s_j = \sum_{k=1}^j N_k b_k \quad \text{and} \quad t_j = \sum_{k=1}^j f_k \quad (j > 1), \quad (4)$$

respectively with $s_0 = 0$ and $t_0 = 0$. The range over the entire polymer for t is $[0, 1]$.

The volume fraction of type- j segments, $\phi_j(\mathbf{r}, \mathbf{u})$, now depends on both spatial and orientational variables (\mathbf{r} and \mathbf{u}), and satisfies

$$\frac{1}{V} \int d\mathbf{r} d\mathbf{u} \phi_j(\mathbf{r}, \mathbf{u}) = f_j. \quad (5)$$

The variation of $\phi_j(\mathbf{r}, \mathbf{u})$ gives rise to a microstructure and is a central focus of a theoretical calculation, which can be used to compare with experimental data. According to (1), the above definition yields a trivial result

$$\frac{1}{V} \sum_{j=1}^m \int d\mathbf{r} d\mathbf{u} \phi_j(\mathbf{r}, \mathbf{u}) = 1. \quad (6)$$

Incompressibility condition

One basic assumption commonly made in studying a polymer melt is the incompressibility condition,

$$\sum_{j=1}^m \int d\mathbf{u} \phi_j(\mathbf{r}, \mathbf{u}) = 1. \quad (7)$$

This imposed condition can be contrasted with the trivial result in eq. (6), and is specified for any \mathbf{r} . Physically, it implies that in a unit volume about \mathbf{r} , multi-component polymer segments fill the space within a given melt density ρ_0 , plugging in from different directions. The volume fraction itself, however, can have a nonuniform direction-dependence, typical for a system that displays a *liquid-crystal* state [23,24].

Wormlike-chain model

Given the configuration of a typical copolymer as indicated by the spatial coordinates $\mathbf{R}(s)$, a unit vector can be define to represent the tangent direction of the curve,

$$\mathbf{u}(s) = \frac{d\mathbf{R}(s)}{ds}. \quad (8)$$

The reduced bending Hamiltonian of a configuration can be written as

$$\begin{aligned} \beta H &= \sum_{j=1}^m \frac{\lambda_j}{2} \int_{s_{j-1}}^{s_j} ds \left| \frac{d\mathbf{u}(s)}{ds} \right|^2 \\ &= \sum_{j=1}^m \frac{\lambda_j}{2Nb_j} \int_{t_{j-1}}^{t_j} dt \left| \frac{d\mathbf{u}(t)}{dt} \right|^2. \end{aligned} \quad (9)$$

The combination λ_j/Nb_j appears in this reduced form.

The entropic contribution to the free energy of such a polymer in a mean field $W_j(\mathbf{r}, \mathbf{u})$ can be obtained from the single-chain partition function Q , where $Q = \int d\mathbf{r} d\mathbf{u} q(\mathbf{r}, \mathbf{u}, 1)/4\pi V$. Instead of integrating over the entire phase space, an equivalent way to obtain Q is to consider the Green's function of the system. The reduced Green's function (often called propagator in polymer theories) $q(\mathbf{r}, \mathbf{u}, t)$ represents the probability of finding a polymer portion with the starting end labeled $t = 0$ and the terminal end labeled t . The terminal end, which is located in the j -th block, is located at a spatial point specified by \mathbf{r} and points at a direction specified by the unit vector \mathbf{u} . As we deductively solve for the propagator by starting from the first block and reaching block- j , we need to solve [25,26]

$$\frac{\partial}{\partial t} q(\mathbf{r}, \mathbf{u}, t) = \left[\frac{Nb_j}{2\lambda_j} \nabla_{\mathbf{u}}^2 - Nb_j \mathbf{u} \cdot \nabla_{\mathbf{r}} - W_j(\mathbf{r}, \mathbf{u}) \right] q(\mathbf{r}, \mathbf{u}, t), \quad (10)$$

which is subject to the initial condition $q(\mathbf{r}, \mathbf{u}, t = 0) = 1$. Note that for block- j , a dimensionless flexibility parameter can be defined as

$$\alpha_j \equiv \frac{Nb_j}{2\lambda_j}, \quad (11)$$

shown in this equation as a combination. Due to the distinct ends for multi-block copolymers, complementary to $q(\mathbf{r}, \mathbf{u}, t)$ is the propagator $q^*(\mathbf{r}, \mathbf{u}, t)$, now for a polymer segment of length $1 - t$, with one terminal end labeled by t and another $t = 1$. It represents the probability of finding the t -terminal, which is at the spatial position specified

by \mathbf{r} and points in a direction specified by the unit vector $-\mathbf{u}$. This propagator satisfies a similar equation

$$\frac{\partial}{\partial t} q^*(\mathbf{r}, \mathbf{u}, t) = \left[-\frac{Nb_j}{2\lambda_j} \nabla_{\mathbf{u}}^2 - Nb_j \mathbf{u} \cdot \nabla_{\mathbf{r}} + W_j(\mathbf{r}, \mathbf{u}) \right] q^*(\mathbf{r}, \mathbf{u}, t), \quad (12)$$

which is subject to the initial condition $q^*(\mathbf{r}, \mathbf{u}, 1) = 1$.

Free energy

Performing the Hubbard-Stratonovich transformation and taking the saddle-point approximation [2], we arrive at a reduced mean-field Helmholtz free energy per chain,

$$\beta F = -\ln Q - \frac{1}{V} \int d\mathbf{r} d\mathbf{u} \sum_{j=1}^m W_j(\mathbf{r}, \mathbf{u}) \phi_j(\mathbf{r}, \mathbf{u}) + \beta H_{\text{int}}, \quad (13)$$

where H_{int} is the total interaction energy. At the level of saddle-point approximation, the free-energy functional needs to be minimized with respect to all involved functions, to be stated below. In the most general case, the interaction between two segments in the system has both spatial and orientational dependencies. Within the second virial-coefficient treatment, the interaction energy per chain can be written as

$$\begin{aligned} \beta H_{\text{int}} &= \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' d\mathbf{u} d\mathbf{u}' \sum_{i,j} K_{ij}(\mathbf{r}, \mathbf{u}; \mathbf{r}', \mathbf{u}') \\ &\quad \times \phi_i(\mathbf{r}', \mathbf{u}') \phi_j(\mathbf{r}, \mathbf{u}), \end{aligned} \quad (14)$$

where K_{ij} is a kernel function that is specified in a particular model for species i and j .

The free energy, which is a functional of $\phi_j(\mathbf{r}, \mathbf{u})$ and $W_j(\mathbf{r}, \mathbf{u})$, must be minimized with respect to these functions to close the self-consistency, required by the saddle-point condition. The incompressibility condition, eq. (7), is normally dealt with by the introduction of a Lagrange multiplier at that stage and added to the minimized functional.

MS and FH free energies

For an orientationally anisotropic system, which is our mainly concern here, an orientational order-parameter tensor for component j can be introduced as

$$\mathbf{Q}_j(\mathbf{r}) = \frac{3}{2} \int d\mathbf{u} \left(\mathbf{u} \mathbf{u} - \frac{\mathbf{I}}{3} \right) \phi_j(\mathbf{r}, \mathbf{u}), \quad (15)$$

where \mathbf{I} is a 3×3 second-rank unit tensor. The degree of alignment of molecules can be measured by the largest eigenvalue of the tensor \mathbf{Q} . In a situation where segments are perfectly aligned, this eigenvalue is equal to unity; whereas in a situation where orientations of segments are disordered, this eigenvalue vanishes. Note that the prefactor (3/2) used in eq. (15) is consistent with the definition of the so-called Q -tensor in a liquid crystal theory [27]; in

some polymer references where wormlike-chains are modeled, this prefactor was dropped [18, 28–31].

As a phenomenological approach to deal with the orientational ordering, the MS approximation amounts to taking the orientational part of the mean field in the form

$$W_j(\mathbf{r}, \mathbf{u}) = \bar{W}_j(\mathbf{r}) - \frac{3}{2} \mathbf{M}_j(\mathbf{r}) : \left(\mathbf{u}\mathbf{u} - \frac{\mathbf{I}}{3} \right), \quad (16)$$

where \mathbf{M}_j is a 3×3 second-rank tensor field which is conjugated to \mathbf{Q}_j . Without losing generality, the orientationally averaged $\bar{W}_j(\mathbf{r})$, which is a function of \mathbf{r} only, is denoted by $W_j(\mathbf{r})$ below.

Thus, the free energy per chain is written as

$$\begin{aligned} \beta F = & -\ln Q - \frac{1}{V} \int d\mathbf{r} \sum_{j=1}^m [W_j(\mathbf{r}) \phi_j(\mathbf{r}) \\ & - \mathbf{M}_j(\mathbf{r}) : \mathbf{Q}_j(\mathbf{r})] + \beta H_{\text{int}} \\ & + \frac{1}{V} \int d\mathbf{r} \xi(\mathbf{r}) \left[\sum_{j=1}^m \phi_j(\mathbf{r}) - 1 \right], \end{aligned} \quad (17)$$

where ξ is the Lagrange multiplier which is imposed to retain the incompressibility condition. At the same level of the MS approximation for the orientational dependence and the local FH interaction approximation, the interaction energy is approximated by [32, 33]

$$\begin{aligned} \beta H_{\text{int}} = & \frac{1}{2V} \sum_{i \neq j} \chi_{ij} N \int d\mathbf{r} \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) \\ & - \frac{1}{3V} \sum_{i,j} \mu_{ij} N \int d\mathbf{r} \mathbf{Q}_i(\mathbf{r}) : \mathbf{Q}_j(\mathbf{r}). \end{aligned} \quad (18)$$

Within this free energy, these are typical parameters and expressions appearing in a SCFT formalism, regardless of the statistics used to describe the nature of the copolymers (Gaussian *versus* wormlike). Here, χ_{ij} is the FH parameter, and μ_{ij} is the MS parameter for species i and j .

The free energy functional, eq. (17), needs to be minimized with respect to all five types of fields, $\phi_j(\mathbf{r})$, $W_j(\mathbf{r})$, $\mathbf{Q}_j(\mathbf{r})$, $\mathbf{M}_j(\mathbf{r})$, and $\xi(\mathbf{r})$. This leads to

$$W_j(\mathbf{r}) = \sum_{i \neq j} \chi_{ij} N \phi_i(\mathbf{r}) + \xi(\mathbf{r}), \quad (19)$$

$$\phi_j(\mathbf{r}) = \frac{1}{4\pi Q} \int_j d\mathbf{u} dt q(\mathbf{r}, \mathbf{u}, t) q^*(\mathbf{r}, \mathbf{u}, t), \quad (20)$$

$$\mathbf{M}_j(\mathbf{r}) = \frac{2}{3} \sum_{i=1}^m \mu_{ij} N \mathbf{Q}_i(\mathbf{r}), \quad (21)$$

$$\mathbf{Q}_j(\mathbf{r}) = \frac{1}{4\pi Q} \int_j d\mathbf{u} dt \left[\frac{3}{2} \mathbf{u}\mathbf{u} - \frac{\mathbf{I}}{2} \right] q(\mathbf{r}, \mathbf{u}, t) q^*(\mathbf{r}, \mathbf{u}, t), \quad (22)$$

and

$$\sum_{j=1}^m \phi_j(\mathbf{r}) = 1. \quad (23)$$

Equations (19)–(23), together with eqs. (10) and (12) form a consistent set of equations in a typical SCFT formalism within the MS approximation.

Independent parameters in the model

We now assess the number of independent parameters in the current SCFT formalism that is established generally for an m -block polymer melt.

1) Volume fractions. There are m volume fractions $f_i (i = 1, \dots, m)$. Because of the normalization in eq. (1), in total the system has $m-1$ independent volume fractions as parameters.

2) Flory-Huggins parameters. There are $m(m-1)/2$ FH parameters, appearing in the formalism as combinations $\chi_{ij} N$, where $i \neq j$.

3) Flexibility constants. In total, there are m different flexibility constants α_j defined in eq. (11) and appearing in eqs. (10) and (12). If we use L to reduce all length-related variables, the other combination that appears in these equations is Nb_j/L . There are in total $m-1$ independent parameters of such type, with the consideration of the normalization condition in (2).

4) Maier-Saupe parameters. Because the MS interaction is also defined for the same species, there are $m(m+1)/2$ MS parameters, appearing in the formalism as combinations $\mu_{ij} N$.

In summary, a grand total of $G = m^2 + 3m - 2$ independent parameters exist in a problem of multiblock copolymers which has m distinct species of blocks. Next we examine a few special cases.

Homopolymer liquid-crystal problem

In this single-component problem, $m = 1$ and $G = 2$, one has a single MS parameter μN together with $\alpha = Nb/2\lambda = L/2\lambda$ as another parameter. In refs. [34–36], 2λ is selected as the effective Kuhn length a as a basic unit, hence the flexibility parameter becomes the degree of polymerization L/a in the large L/a limit. In a related lyotropic liquid-crystal problem where the MS term is replaced by the Onsager energy [37], the MS coefficient is replaced by the coefficient of the Onsager interaction [23, 38, 39]. The limits $L/a \gg 1$ and $L/a \ll 1$ correspond to MS theories or Onsager theories for flexible and rodlike chains. This is a two-parameter theory.

Conformationally symmetric AB diblock copolymers

In this case $m = 2$. The conformation symmetry refers to the case where b_j , λ_j , and $\mu_j N$ are i -independent. Here is another special case in which we can take $\alpha = Nb/2\lambda =$

L/a as an independent parameter. In an isotropic problem, $\mu_j N = 0$, the relevant parameters are hence, f (of the A-component for example), χN , and L/a . Thus we have a three-parameter theory which can be contrasted with SCFT of the same problem based on a Gaussian-chain model, in which f and χN are the natural choice of the parameters. The ratio L/a measures the semiflexibility of the polymers, enters into a wormlike-chain model naturally.

At a special case $f = 0.5$ (for the lamellar phase), the physical properties such as the order-disorder transition, the unit-cell size and the interfacial width were investigated by using numerical techniques or the random-phase approximation, in refs. [12, 15, 40]. The three-parameter theory at any f is solved in refs. [16, 41] which explore the three-dimensional morphologies formed in this system. In refs. [15, 16, 40, 41], b is implicitly assumed to be the same as a , the basic statistical measure, hence χN is directly written as $\chi L/a$. This is unnecessary, as we can keep using χN and the exactly same theoretical results can emerge.

Accounting for the effects of the orientational interactions between segments, in the case of $\mu_{ij} = \mu$, Netz and Schick focused on calculating the phase diagram of symmetric diblocks, $f = 0.5$ [29]. The general problem of nematic diblock copolymers, however, is not systematically solved yet. In this case it has four independent reduced parameters f , χN , L/a , and μN .

Conformationally symmetric AB wormlike polymer blends

A system that is closely related to the last one is the demixing of AB homopolymers that form an interface between two immiscible (A- or B-rich) bulk phases. For a conformationally symmetric case, we again have four basic reduced parameters, f , χN , L/a , and μN . This can be contrasted with the Gaussian-chain problem which has two basic reduced parameters f and χN ; Helfand's analytical solution to the *compositionally* symmetric case ($f = 1/2$) is a classical milestone in polymer theory [42]; the significance of composition asymmetry ($f \neq 1/2$) on the interface profile in such a simple problem was explored following that work, mostly by numerical methods, in terms of f and χN .

Returning to the wormlike chains, a four-parameter problem, we wish to point out that the theory is not completely solved, but will predict a number of interesting features in liquid-crystal interface composed of two types of molecules. This will help us to understand the interplay between and the merging of polymer-demixing interface and liquid-crystal interface. The reduced two-parameter problem where $f = 1/2$ and $\mu N = 0$, was indeed examined in refs. [13, 14]; the effects of orientation-position coupling in the vicinity of the AB polymer interface were illustrated, even though there is no explicit orientation-orientation interaction.

Rod-coil diblock copolymers, isotropic phases

Here we have an extreme example of conformational-*asymmetric* diblock copolymer problems ($m = 2$). Based on the general analysis above, we need one volume fraction parameter, f (of the A-component for example) and one FH parameter χN . To stay in the isotropic-phase regime, it is adequate to let $\mu N = 0$. The flexibility $\alpha_R = Nb_R/2\lambda_R$ on the rodlike (R) block now vanishes because of the $\lambda_R \rightarrow \infty$ limit. The other two remaining parameters in the theory are the flexibility parameter $\alpha_C = Nb_C/2\lambda_C$ of the coil (C) block, which can be large (true rod-coil case) and small (crossing over to rod-worm case), and the ratio b_C/b_R (here Nb_{RB} is used to reduce all spatial variables).

This theory, generally for rod-worm diblock copolymers, contains four parameters, f , χN , and α_C , and b_C/b_R . A special case is pushing the formalism to the asymptotic limit $\alpha_C \gg 1$ which is suitable for the ideal rod-coil case, we can identify $a_C = 2\lambda_C$ on the C block where a_C is the Kuhn length of the coil block. Now, a_C can be used as the reference packing length b_C , $b_C = a_C$, then we simply have $\alpha_C = N$.

One can show that within the asymptotic $\alpha_C \gg 1$ limit, the two parameters α_C and b_C/b_R show up as one single combination b_C^2/Nb_R^2 . The proof of this point can be found in refs. [22] and [43]. Hence for an ideal isotropic rod-coil problem we need to examine the phase space in terms of three reduced parameters f , χN and b_C^2/Nb_R^2 using the current formalism.

On the other hand, the entire rod-coil problem can be reformulated based on SCFT in which the coil block is treated to follow the Gaussian-chain statistics. In such an approach and with the further identification $a_C = b_C$, a conformation parameter $\nu^2 = b_C^2/Nb_R^2$ is used as an independent parameter and one of the two, $(Nb_C^2)^{1/2}$ or Nb_R , is used as a length-rescaling parameter [30, 44, 45]. The equivalence between the parameter set used in three-parameter wormlike-chain SCFT and the set used in three-parameter Gaussian-chain SCFT at the large N limit is transparent here. Beyond the commonly found bcc, lamellar, columnar, and gyroid states, a rod-coil system can display the A15 state in a certain parameter region. A systematic investigation of this problem, in terms of f , χN , and ν^2 (where $N \gg 1$) is presented in ref. [22].

In the intermediate- and small- α_C regime, the formalism is suitable for describing microphase separation occurring in a copolymer melt composed of copolymers that have rodlike and semiflexible-chain blocks (hence rod-worm polymers). The structural properties based on the four-parameter theory containing f , χN , α_C , b_C/b_R (or equivalently expressing the last parameter through ν^2 to retain the theoretical structure of a rod-coil problem) in the intermediate- and small- α_C regime have not been thoroughly explored yet.

Rod-coil diblock copolymers, liquid-crystal phases

To completely map out the entire phase diagram for the rod-coil problem, in principle one needs to add three more parameters, $\mu_{RR}N$, $\mu_{CC}N$, and $\mu_{RC}N$. One can argue that the most dominating one is $\mu = \mu_{RR}$ because the rod blocks can be liquid-crystal-like and ignore μ_{CC} and μ_{RC} . This reduced version is most experimentally relevant.

A four-parameter theory based on the Gaussian-chain model, where the four parameters are f , χN , ν , and μN , has been considered in many studies [30, 45–47]. Life now becomes more complicated. Mostly, because of the complexity of the problem, a sub-regime of the phase space is examined with a reduced dimensionality in spatial variation (with the exception of [47] which considers three dimensions). It has been demonstrated that the rod blocks exclusively play a crucial role in the formation of liquid-crystal domains of various spatial symmetries. Despite of the efforts made to understand a sub-regime of the phase space, a complete understanding based on the four-parameter rod-worm formalism has not emerged yet but is highly desirable.

Due to the advantageous functions in the mechanical and photoelectric properties, semicrystalline block copolymers have recently attracted intensive experimental interest [48–52]. Extensions beyond a four-parameter liquid-crystal rod-coil model to rod-worm, coil-worm, and worm-worm copolymer models can be easily adopted within the current SCFT formalism. Essential parameters are clearly identifiable, as discussed above. To this end, even more parameters need to be introduced and recent studies are limited to, again, a sub parameter space [17–21]. Some liquid crystalline structures with exotic orientational and positional symmetries have been discovered in these studies.

Branched polymers

The topological structure of a multiblock copolymer is another key factor that determines the microphase-separated structure of a melt composed of these polymers. In the above we have not discussed this class of polymers, in which star-branched (fig. 1(b)) and side-branched polymers (fig. 1(c)) are good examples. In order to correctly characterize the branched structures, one needs to utilize a particular strategy [2] to solve eqs. (10) and (12) in analogy to the Feynman-Kac formula in the path-integral description of quantum mechanics [53]. It is worth emphasizing that the number of physical parameters is not affected by the variation of chain topology.

Other parameters

There are other parameters that can significantly affect the final melt structure, which can be included in the aforementioned formalism. Among them, the angles at which the different blocks are attached to each other,

labeled in fig. 1 by red circles, become important in a wormlike-chain problem. These angles are determined by the very chemical bonds that are used to connect different blocks and are less important in a system made of long, flexible polymers, as the angular dependencies are expected to become uncorrelated in a coil-polymer problem. Here for short and rigid polymer wormlike blocks, these angular effects can significantly change the entire physical picture.

Segmental length, Kuhn length, the flexible limit

We started by stating that two length scales, packing length b_j and persistence length λ_j , are required to describe the statistical physics of a semiflexible block j . In the polymer literature, another length scale, the Kuhn length a_j , is often used for a flexible block j ; the Kuhn length appears in the Edwards model as the basic length scale [1].

To clarify, let us now take the coil limit $L_j \gg \lambda_j$ for a polymer in no external field for a moment. Through the classical derivation of Kratky and Porod [54] or the correlation-function derivation of Saito *et al.* [11], we understand that

$$a_j = 2\lambda_j \quad (24)$$

can be established by an examination of the mean-square end-to-end distance $\langle R_j^2 \rangle$ for block j . Thus, one can use $2\lambda_j$ or a_j interchangeably in the wormlike-chain formalism, with the understanding that in the coil limit, $2\lambda_j$ recovers the Kuhn length a_j in a three-dimensional system (however, care needs to be taken for other dimensions [55]). No new length scale is introduced here. In polymer statistics, and indeed in real systems, $\langle R_j^2 \rangle^{1/2}$ and L_j are physical lengths and hence $a_j \equiv \langle R_j^2 \rangle / L_j$ is uniquely defined.

When a wormlike chain is in a weak orientational field [$W_j(\mathbf{r}, \mathbf{u}) \approx W_j(\mathbf{r})$], one can show that (10) reduces to

$$\frac{\partial}{\partial t} \bar{q}(\mathbf{r}, t) = \left[\frac{N b_j a_j}{6} \nabla_{\mathbf{r}}^2 - W_j(\mathbf{r}) \right] \bar{q}(\mathbf{r}, t), \quad (25)$$

for block j in the range $[t_{j-1}, t_j]$ where $\bar{q}(\mathbf{r}, t)$ is the directionally averaged $q(\mathbf{r}, \mathbf{u}; t)$. This equation can be independently derived starting from the Edwards model, in which a_j is a Kuhn length and b_j is a packing length.

Taking conformationally asymmetric, *flexible* diblock copolymers for example, we can use the square root of one of the two combinations ($a_1 b_1$ and $a_2 b_2$) as the length scale to reduce \mathbf{r} . As the result, the theory contains three parameters $f, \chi N, a_1 b_1 / a_2 b_2$ within a Gaussian-chain theory described by (25). One could, though, define N_j through L_j / a_j (hence a different $N = N_1 + N_2$) from the beginning, using a_j as the basic unit rather than b_j ; this gives rise to a coefficient a_j^2 for the ∇^2 -term (that is, b_j disappears from the above equation); now χN must be rewritten to take into account the difference between a_j and

Table 1. Basic melt-systems studied based on the wormlike-chain SCFT formalism. Research work that entirely uses a Gaussian-chain approach is not listed here, although it may be highly applicable in many cases. The word “isotropic” refers to no consideration of the directional ordering of segments. The phrase “conformationally symmetric” refers to identical conformational properties of constituting blocks. Some open theoretical problems are also suggested.

System	Varying parameters	Specified parameters	References
MS theory of the isotropic-nematic transition in wormlike homo-polymers	$\alpha, \mu N$		[34–36]
Isotropic, conformationally and compositionally symmetric AB wormlike polymer blends	α (large), χN	$f = 1/2, \mu N = 0$	[13]
Nematic, conformationally symmetric AB wormlike polymer blends, in general	$f, \chi N, \alpha, \mu N$		[29]; open
Isotropic, conformationally and compositionally symmetric AB wormlike diblock copolymers	$\chi N, \alpha$	$f = 1/2, \mu N = 0$	[12, 15, 40]
Isotropic, conformationally symmetric AB wormlike diblock copolymers	$f, \chi N, \alpha$	$\mu N = 0$	[16, 41]
Nematic, conformationally symmetric AB wormlike diblock copolymers	$f, \chi N, \alpha, \mu N$		open
Isotropic, rod-coil copolymers	$f, \chi N, \nu^2$	$\mu N = 0$	[22]
Nematic, rod-coil copolymers	$f, \chi N, \nu^2, \mu N$		open
Isotropic, rod-worm copolymers	$f, \chi N, \alpha, \nu^2$	$\mu N = 0$	open
Nematic, worm ₁ -worm ₂ copolymers in general	$f, \chi N, \alpha_1, \alpha_2, \nu^2, \mu_{ij} N$		[17–21]; open

b_j , such that N needs to be rescaled within the combination χN by reference to monomer volume densities [56]. Regardless of which set of parametrization to use, there are only three combinations of parameters. Adopting the notations in this paper, we can re-express the phase diagrams calculated by Vavasour and Whitmore [56], Matsen and Schick [57], as well as Matsen and Bates [58], in terms of $f, \chi N, a_1 b_1 / a_2 b_2$ for a $b_1 \neq b_2$ system, generally.

To study the properties of a multicomponent *flexible* polymer melt composed of conformationally symmetric blocks ($a_j = a$ and $b_j = b$), in the literature it is customary to directly take a as the packing length scale, $b = a$, which is possible because only one packing length is needed. If one insists on using $b \neq a$, the only slight complication is the definition of monomer size hence N , which in turn has an effect on the definition of χ through the combination χN . Using $b = a$ or $b \neq a$, re-scaling can be trivially done here.

Summary

The Flory-Huggins mixing free energy of a polymer melt stems from the basic physical idea of packing different species of monomers. The Maier-Saupe free energy is another commonly used approximation to deal with the orientational ordering in liquid-crystal systems. Using the same concepts and considering the fact that melts formed by wormlike chains are directionally dependent on persistence lengths, we emphasize here the number of reduced parameters that need to be considered in a general theory. Within the same theoretical framework, the usefulness of this formalism in understanding basic poly-

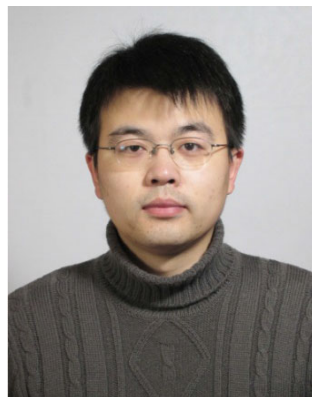
mer systems is briefly reviewed by using a few examples: isotropic-nematic liquid crystal transition, AB homopolymer interface, and microstructures in AB diblock copolymers as well as rod-coil copolymers. Some of the basic systems are listed in table 1. We wish that this Perspective paves the way for further structural determinations of other wormlike polymer mixtures, in which the polymer semiflexibility is considered as a tuning parameter.

The SCFT approach is a general method that can be used as a mean-field-level approximation for polymer melts composed of polymers that can be either described by Gaussian- or wormlike-chain statistics. We devote this Perspective to showcase the versatility and power of the wormlike-chain formalism, which can be reduced to a Gaussian-chain formalism in appropriate parameter regimes. The latter, although now asymptotically limited to systems containing flexible chains, is mathematically easier to handle as it only uses \mathbf{r} as a variable for spatially inhomogeneous systems. Solving the above-listed wormlike-chain SCFT equations is obviously more challenging mathematically, as now both \mathbf{r} - and \mathbf{u} -dependencies are required. Many recent efforts have been made to develop numerical approaches that can be efficiently used to tackle the differential equations in the formalism. Recent developments in computational algorithms for this area of research are reviewed in table I and the corresponding text of ref. [41].

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